Gas-Phase Photoelectron Spectroscopic and Theoretical Studies of 1,2-Dichalcogenins: Ionization Energies, Orbital Assignments, and an Explanation of Their Color

Richard S. Glass,*,[†] Nadine E. Gruhn,[†] Dennis L. Lichtenberger,[†] Edward Lorance,[†] John R. Pollard,[†] Marc Birringer,[‡] Eric Block,[‡] Russell DeOrazio,[‡] Chunhong He,[‡] Zhixing Shan,[‡] and Xing Zhang[‡]

Contribution from the Departments of Chemistry, The University of Arizona, Tucson, Arizona 85721, and State University of New York at Albany, Albany, New York 12222

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Abstract: Gas-phase photoelectron spectroscopy and theoretical calculations are used to study the electronic structure of 1,2-dichalcogenins. Photoelectron spectra are reported for 1,2-dithiin, 3,6-dimethyl-1,2-dithiin, 3,6-diisopropyl-1,2-dithiin, 3,6-di-*tert*-butyl-1,2-dithiin, 2-selenathiin, 1,2-diselenin, 3,6-dimethyl-1,2-diselenin, and 3,6-di-*tert*-butyl-1,2-diselenin and are assigned on the basis of (a) trends in ionization cross sections as the ionization photon energy is varied and (b) shifts of the ionizations as chemical substitutions are made. The calculated properties of 1,2-dithiin and 3,6-dimethyl-1,2-dithiin are compared to experimental results. The first four filled frontier valence orbitals are associated with orbitals that can be described as being primarily carbon π and chalcogen lone pair in character. Comparison of spectra collected with He I, He II, and Ne I ionization sources for each compound indicate that there is a large degree of mixing of chalcogen and carbon character through most of the valence orbitals. The highest occupied molecular orbital of the selenium-containing compounds has more chalcogen character than the highest occupied molecular orbital of the 1,2-dithiins. The photoelectron spectra of 1,2-dithiin and 1,2-diselenin contain a sharp ionization that corresponds to removal of an electron from an orbital that is predominantly chalcogen−chalcogen σ bonding in character. The narrow ionization profile indicates fairly weak chalcogen−chalcogen σ bonding in this orbital, which would result in a corresponding weakly antibonding chalcogen−chalcogen σ^* orbital. Computational results show that an orbital that is primarily S−S σ^* in character is the lowest unoccupied molecular orbital of 1,2-dithiin, and electronic transition calculations show a low-energy HOMO-to-LUMO transition that can be described as a π/lone pair-to-σ^* transition that explains the unusual color of 1,2-dichalcogenins.

Introduction

1,2-Dithiins, **1**, have attracted considerable interest for several reasons. Thiarubrine A, **1a**, thiarubrine B, **1b**, and related compounds occur naturally in plants such as those of the *Compositae* (*Asteraceae*) family.[1,2] They show a wide range of biological activity both in the dark and in the light, including potent antifungal, antibacterial, antitumor, and nematocidal activity.[3] The dithiin ring is a theoretically interesting 8π-electron antiaromatic system that has been studied computationally.[3−12]

Despite the absence of a normal chromophore, 1,2-dithiins are brightly colored reddish-orange compounds that absorb in the visible near 450 nm. An early quantum mechanical calculation[4] assigned the visible transitions in the spectrum of 1,2-dithiin to a weak π-to-π^* transition, but this calculation used a planar geometry that is unreliable, given the twisted geometry of 1,2-dithiin revealed by the microwave spectrum[13] and later calculations.[8−12] A more recent ab initio study[8] using the variation-perturbation CIPSI method calculated the energy of the first excited singlet states of 1,2-dithiin and assigned the visible transition to a ^{1}B (HOMO to LUMO) transition, but no explanation has been given for the unusual energy of this transition.

This paper reports gas-phase photoelectron spectroscopic and theoretical studies of the electronic structure of 1,2-dichalcogenins, whose synthesis and electrochemistry are the subjects

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* To whom correspondence should be addressed.

[†] The University of Arizona.

[‡] State University of New York at Albany.

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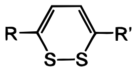
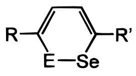
of the accompanying paper.[14] The gas-phase photoelectron spectra of 1,2-dithiin (**1c**) and several substituted 1,2-dithiins (**1d**−**f**) are compared to evaluate the effect that substituents have upon the electronic structure. In addition, the photoelectron spectra of 2-selenathiin (**2a**), 1,2-diselenin (**2b**), 3,6-dimethyl-1,2-diselenin (**2c**), and 3,6-di-*tert*-butyl-1,2-diselenin (**2d**) are studied to determine what effect changing the chalcogen atom from sulfur to selenium has upon the electronic structure of these molecules. As will be described, the photoelectron spectra of 1,2-dithiin and 1,2-diselenin contain an ionization from an orbital that is predominantly chalcogen−chalcogen σ bond in character and is weakly bonding. This weak chalcogen−chalcogen σ bond orbital is expected to result in a low-lying orbital of primarily chalcogen−chalcogen σ* character. Calculations on 1,2-dithiin confirm this expectation and indicate that this chalcogen−chalcogen σ* orbital is associated with a transition in the visible region of the absorption spectrum.



1a, R = CH$_2$=CHC≡C-C≡C-
R′ = MeC≡C-
1b, R = CH$_2$=CHC≡C-
R′ = MeC≡C-C≡C-
1c, R = R′ = H
1d, R = R′ = Me
1e, R = R′ = *i*-Pr
1f, R = R′ = *t*-Bu



2a, E = S, R = R′ = H
2b, E = Se, R = R′ = H
2c, E = Se, R = R′ = Me
2d, E = Se, R = R′ = *t*-Bu

Experimental Section

Photoelectron Spectroscopy. Gas-phase photoelectron spectra were recorded using an instrument that features a 36-cm, 8-cm gap hemispherical analyzer (McPherson) and custom designed sample cells, discharge source, and detection and control electronics[15] that have been described in more detail elsewhere.[16] The excitation source was a quartz lamp with the ability, depending on operating conditions, to produce Ne I (16.85 eV), He I (21.21 eV), or He II (40.8 eV) photons. For the He I and He II experiments, the ionization energy scale was calibrated using the $^{2}\mathrm{E}_{1/2}$ ionization of methyl iodide (9.538 eV), with the Ar $^{2}\mathrm{P}_{3/2}$ ionization (15.759 eV) used as an internal energy scale lock during data collection. For Ne I experiments, the Xe $^{2}\mathrm{P}_{3/2}$ ionization (12.130 eV) was used as the internal energy scale lock. During He I and He II data collection the instrument resolution, measured using the full-width-at-half-maximum of the Ar $^{2}\mathrm{P}_{3/2}$ ionization, was 0.015−0.025 eV. During Ne I data collection the instrument resolution, measured using the full-width-at-half-maximum of the Xe $^{2}\mathrm{P}_{3/2}$ ionization, was 0.020−0.026 eV. All data are intensity-corrected with an experimentally determined instrument analyzer sensitivity function that assumes a linear dependence of analyzer transmission (intensity) to the kinetic energy of the electrons within the energy range of these experiments.

All of the spectra were corrected for the presence of ionizations from secondary photons in the discharge sources.[17] The He I spectra were corrected for ionizations from He Iβ photons (1.9 eV higher in energy, and 3% the intensity of the He Iα photons), the He II spectra were corrected for He IIβ photons (7.568 eV higher in energy, and 12% the intensity of the He IIα photons), and the Ne I spectra were corrected for spin−orbit splitting of the Ne I source, which produces photons 0.18 eV lower in energy and 15% the intensity of the primary Ne I photons.

All of the compounds studied are light and temperature sensitive, and were handled at low temperature to limit self-polymerization. Liquid samples were frozen and loaded into a sample cell that had been cooled in a −40 °C freezer. The cell was then placed in the instrument and allowed to slowly warm, and the spectra were collected at the temperature (monitored using a "K"-type thermocouple passed through a vacuum feedthrough and attached directly to the sample cell) where sufficient sample vapor pressure was achieved. The temperatures at which data were obtained are (10^{-4} Torr): 1,2-dithiin, 7−10 °C; 3,6-dimethyl-1,2-dithiin, 4−8 °C; 3,6-diisopropyl-1,2-dithiin, −15−8 °C; 3,6-dimethyl-1,2-dithiin, −20−5 °C; and 3,6-di-*tert*-butyl-1,2-diselenin, 25−35 °C. 3,6-Di-*tert*-butyl-1,2-dithiin is a solid that was loaded into the cell at room temperature, and spectra were collected at 24−34 °C. A sample of 2-selenathiin was prepared in a matrix of frozen hexadecane (to slow self-polymerization)[14,18] and run from a sample cell that had been cooled in dry ice for several hours and allowed to slowly warm in the instrument as described for the neat liquid samples with data obtained at temperatures of −25 to −10 °C. Data were also collected on 1,2-dithiin from a hexadecane matrix to ensure that this method gave spectra comparable to those collected on a neat liquid. Data were collected for 1,2-dithiin in this manner at temperatures of −10 to 0 °C and gave an identical spectrum to that collected from the neat liquid, although the spectrum was partially obscured above 11 eV due to the presence of ionizations from the small amount of hexadecane present in the gas phase at these temperatures. Spectra of 1,2-diselenin were collected by placing about 5 mL of a solution of 1,2-diselenin in pentane (7.7 mg/mL) in a glass tube with a Teflon stopcock that was attached to a needle valve by a Swagelock glass to metal connection (Teflon ferrule). The pentane was removed by vacuum in a dry ice/ethanol bath (−72 °C), and after all traces of pentane were gone, the tube was allowed to warm until the spectrum of 1,2-diselenin was observed.

Data Analysis. In the figures of the data, the vertical length of each data mark represents the experimental variance of that point.[19] The valence ionization bands are represented analytically with the best fit of asymmetric Gaussian peaks.[19] The bands are defined with the position, amplitude, halfwidth for the high binding energy side of the peak, and the halfwidth for the low binding energy side of the peak. The peak positions and halfwidths are reproducible to about ±0.02 eV (∼3σ level). Confidence limits for the relative integrated peak areas are about 5%, with the primary source of uncertainty being the determination of the baseline, which is caused by electron scattering and taken to be linear over the small energy range of these spectra. The total area under a series of overlapping peaks is known with the same confidence, but the individual peak areas are more uncertain. The fitting procedures used are described in more detail elsewhere.[19]

Computational Methodology. Computations were carried out on an SGI Origin 2000 32-processor mainframe using a single processor under the IRIX64 6.4 operating system using Gaussian 94 (revision E.2).[20] Spartan 4.0.2 GL running on an SGI IRIS workstation under the IRIX 3 operating system was used to visualize molecular orbitals. Calculations on unsubstituted 1,2-dithiin were performed using Hartree−Fock methods, both with and without second-order Møller−Plesset perturbation corrections, and also by the Becke 3−Perdew−Wang 91 hybrid density functional method. All possible variations of the 6-31G and 6-311G basis sets were used [with no polarization functions, heavy atom polarization functions (*), or all atom polarization functions (**), and no diffuse functions, heavy atoms diffuse functions (+), or all atom diffuse functions (++)], as well as the Los Alamos National Labora-

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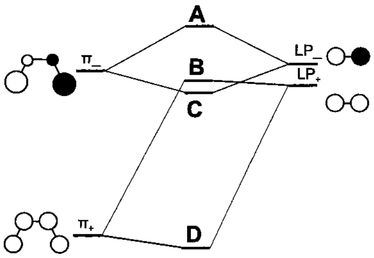

Figure 1. Qualitative molecular orbital diagram describing the carbon π and sulfur lone pair-based orbitals of a 1,2-dithiin in terms of the orbitals of butadiene and disulfide fragments.

tories valence double-ζ basis set with relativistic effective core potentials (LANL2DZ).[21] Upon comparison of these results with experimental geometric parameters obtained from microwave data[13] and experimentally determined ionization potentials, the MP2/6-31+G* method/basis set combination was chosen for use with 3,6-dimethyl-1,2-dithiin.

The neutral species was geometry optimized for both the parent and dimethyl compound. Single-point calculations were made for the cation radical at the neutral species optimized geometry; this method yields much more reliable ionizations potentials (ΔSCF) than Koopmans' theorem. Vibrational frequencies of the ground state of 1,2-dithiin were calculated by RHF/6-31+G* at the RMP2 geometry (no imaginary frequencies, verifying a valid geometry approximation).

Calculations of the electronic transitions of 1,2-dithiin and dimethyl disulfide were performed using the single-excitation configuration interaction method[22] and the 6-31+G* basis set. Geometry optimizations were performed on the S_1 states by CIS/6-31+G* and on the T_1 states by UMP2/6-31+G*. Vibrational frequencies were calculated for the S_1 states by CIS/6-31+G* at the CIS geometry and for the T_1 states by UHF/6-31+G* at the UMP2 geometry. No imaginary frequencies were found for the UHF approximation.

General Electronic Structure of 1,2-Dichalcogenins

The lowest-energy valence ionizations of 1,2-dichalcogenin compounds are expected to be associated with orbitals of primarily carbon π and sulfur or selenium lone pair character. To understand the general electronic structure of the frontier valence orbitals of a 1,2-dichalcogenin, it is helpful to consider the interactions possible between the filled π orbitals of a 1,3-diene fragment and the lone pair orbitals of a dichalcogen fragment as shown in the qualitative molecular orbital diagram in Figure 1. Of course, due to the fact that these molecules are twisted, there will be some mixture of primarily σ type orbitals with the π/lone pair orbitals, but this simple picture will give a starting point for the discussion of the electronic structure of the molecules studied here. The relative energies of the fragment orbitals are based on the energies of the π-based ionizations of 1,3-butadiene and the sulfur lone pair ionizations of dimethyl disulfide.[23] On the right-hand side of this diagram are shown the symmetric (LP_+) and antisymmetric (LP_-) combinations of sulfur lone pair orbitals, where the + or − indicates if the orbital is symmetric or antisymmetic with respect to a pseudo-mirror plane. In the photoelectron spectrum of dimethyl disulfide, the sulfur lone pair ionizations are split in energy by approximately 0.25 eV. In the same general energy region is the one-node π orbital (π_-) of the butadiene fragment as shown on the left side of this diagram. The completely symmetric π orbital (π_+) of the butadiene fragment is much lower in energy than the other three fragment orbitals shown.

The butadiene orbital labeled π_- has the proper symmetry to interact with the sulfur lone pair orbital labeled LP_-. These two fragment orbitals are close to each other in energy, and due to this good energy matching the two molecular orbitals (**A** and **C** in the figure) resulting from the interaction of the two fragment orbitals will be split in energy. On the other hand, while the butadiene fragment orbital π_+ has the proper symmetry to interact with the sulfur lone pair orbital labeled LP_+, the energy difference between these two fragment orbitals is much larger than for π_- and LP_-, and the resultant molecular orbitals (**B** and **D** in the figure) will remain fairly close to the energy of the fragment orbital of similar character. A small amount of character from the unfilled butadiene orbital (LUMO; not shown), which has two nodes and the proper symmetry to interact with LP_+, would also be expected but, due to the very poor energy matching between this high-energy virtual orbital and the filled orbitals, this contribution will be very small.

The overall result from this qualitative description is that the filled orbitals which are a mix of π and lone pair character are expected to fall in a 1:2:1 pattern. Electronic structure calculations, which will be discussed in further detail in the Results section, also give results that agree with this general description of the first filled frontier orbitals. The first four orbitals are calculated to also fall in a 1:2:1 pattern, although the calculations do predict a different ordering of the orbitals **B** and **C** than shown in Figure 1 for 1,2-dithiin. The main point, however, is that these two orbitals are close in energy to one another. As will be shown, substituents can also affect the relative energy of orbitals **B** and **C**.

Photoelectron Results

General Considerations. In this section the observations that support the assignments of the photoelectron spectra will be explained, and calculations will be described in the next section. The most important experimental results are analyzed in further detail in the Discussion section.

The photoelectron spectra of selected 1,2-dithiins collected with a He I source from 6 to 15.5 eV are shown in Figure 2. The parameters used to analytically represent the spectra in subsequent figures with asymmetric Gaussians are shown in Table 1. In addition to evaluating spectra collected with a He I source, making comparisons to spectra collected with He II or Ne I ionization sources can give an indication of the relative amount of chalcogen or carbon character in the orbitals associated with particular ionizations. Photoelectron spectra obtained with different ionization sources differ only in the relative intensities of the ionization bands due to the different inherent photoionization cross-sections of atomic orbitals, which vary as the incident photon energy changes. From theoretical estimates,[24] the photoionization cross section of C 2p orbitals *increase* by a factor of 2.6 as compared to S 3p orbitals when comparing spectra from He II and He I sources, while the photoionization cross section of C 2p orbitals *decrease* by a factor of 2.5 as compared to S 3p when comparing spectra from Ne I and He I sources. Similarly, the cross section of C 2p orbitals *increase* by a factor of 5 as compared to Se 4p orbitals when comparing spectra from He II and He I sources, while the cross section of C 2p orbitals *decrease* by a factor of only 1.5 as compared to Se 4p when comparing spectra from Ne I and He I sources. For ionizations from molecular orbitals, changes in intensity are directly related to the cross section of the atomic orbitals constituting the molecular orbitals (the Gelius model)[25] and give an indication of the origin of an ionization

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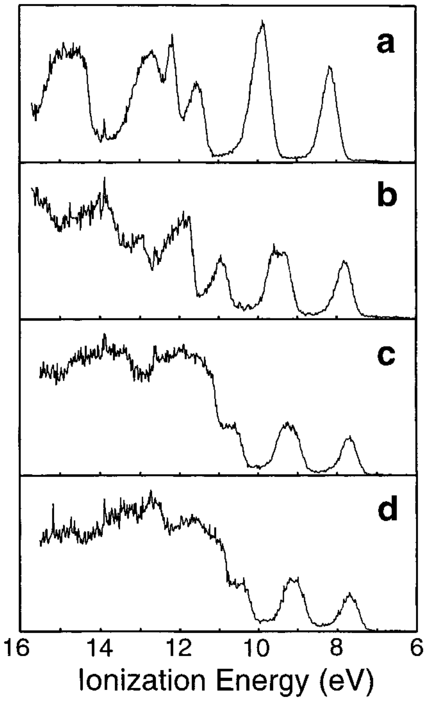

Figure 2. Gas-phase photoelectron spectra collected with a He I source of (a) 1,2-dithiin, (b) 3,6-dimethyl-1,2-dithiin, (c) 3,6-diisopropyl-1,2-dithiin, and (d) 3,6-di-*tert*-butyl-1,2-dithiin.

as well as the amount of mixing of atomic character in the molecular orbitals from which particular ionizations arise. Comparison of He I and He II spectra has been shown to be very useful in the assignment of the aryl π and sulfur lone pair ionizations in the photoelectron spectra of aryl-containing organosulfur compounds.[26] Previous evaluation of the He I and Ne I spectra of several organosulfur compounds has demonstrated that the general trends predicted by the theoretical Ne I photoionization cross section are accurate, indicating that any additional influences to the intensity of ionizations from autoionizations or resonance that might be associated with a low-energy source are insignificant.[16,27] While changes in relative area as the source energy is varied can be used to give an indication of carbon and chalcogen character, it must be remembered that in these cases where a large amount of atomic character mixing is present in the molecular orbitals, only insignificant changes may be observed, especially if there are two ionizations close to each other that partially overlap.

1,2-Dithiin. The photoelectron spectra of 1,2-dithiin collected using Ne I and He II sources are compared in Figure 3. The general features of these spectra are similar to those described previously.[10] The first ionization is a band with a vertical ionization energy of 8.16 eV. For comparison, the first ionization of dimethyl disulfide is 8.96 eV, while the first ionization of the peri-chalcogen-bridged naphthalene naphtho[1,8-*c*,*d*]-1,2-dithiole is located at 7.14 eV.[28] For 1,2-dithiin, more structure is observed in these spectra than in those previously studied.[10] The ratio of relative area of the entire second band to that of the first is approximately 2:1, which would suggest that ionizations from two separate orbitals are under this second band. The evidence of two separate ionizations in this band is stronger for the 3,6-disubstituted molecules to be discussed shortly, for which it is observed that the two ionizations are further split in energy and change the shape of this band. The second ionization band needs to be fit with two Gaussians to give a good analytical representation, and Gaussians 2 and 3 in Figure 3 each are assigned to a separate ionization.

Table 1. Analytical Representations and Assignments of Photoelectron Data

label	assignment	position (eV)	width (eV)	relative area		
				He I	He II	Ne I
1,2-Dithiin						
1	A	8.16	0.46	1	1	
2	B	9.82	0.40	0.96	0.86	
3	C	10.06	0.50	0.72	1.05	
4	D	11.51	0.53	0.91	1.26	
5	S−S σ	12.17	0.26	0.55	0.34	
6	S−C σ	12.66	0.75	1.70	2.15	
7	S−C σ	13.15	0.75	0.50	1.10	
8	C−C, C−H σ	14.40	0.44	0.86	1.27	
9	C−C, C−H σ	14.97	0.88	2.00	2.67	
3,6-Dimethyl-1,2-dithiin						
1	A	7.78	0.46	1	1	
2	C	9.31	0.42	1.02	1.05	
3	B	9.63	0.36	0.64	0.50	
4	D	10.93	0.52	1.06	1.06	
3,6-Diisopropyl-1,2-dithiin						
1	A	7.67	0.46	1	1	1
2	C	9.01	0.38	0.69	0.85	0.83
3	B	9.34	0.44	0.99	0.88	1.04
3,6-*tert*-Butyl-1,2-dithiin						
1	A	7.65	0.46	1		1
2	B	8.93	0.36	0.82		1.12
3	C	9.21	0.39	0.84		0.84
2-Selenathiin						
1	A	8.03	0.43	1	1	1
2	B	9.56	0.37	0.81	1.07	0.95
3	C	9.90	0.43	0.69	0.82	0.62
1,2-Diselenin						
1	A	7.93	0.39	1	1	
2	B	9.38	0.32	0.51	0.53	
3	C	9.60	0.50	0.94	1.82	
4	D	11.22	0.45	0.83	1.34	
5	Se−Se σ	11.61	0.30	0.63	0.57	
6	Se−C σ	12.03	0.88	2.07	2.66	
7	C−C, C−H σ	14.19	0.83	2.50	2.86	
8	C−C, C−H σ	15.01	0.89	0.90	0.49	
3,6-Dimethyl-1,2-diselenin						
1	A	7.64	0.38	1	1.00	
2	C	8.94	0.35	0.85	1.40	
3	B	9.20	0.34	0.65	0.85	
4	D	10.63	0.47	0.89	1.30	
3,6-*tert*-Butyl-1,2-diselenin						
1	A	7.52	0.40	1	1	
2	B	9.60	0.34	0.72	1.28	
3	C	8.84	0.38	0.78	1.23	

The spectrum of 1,2-dithiin does not contain resolved fine structure on the ionizations as has been observed for many aromatic compounds such as benzene.[17] The first ionization of benzene is from the e_{1g} symmetry π orbital and has a very complex shape. In addition to some Jahn−Teller splitting of the $^2E_{1g}$ ion state, there are also two separate resolved vibrational progressions. Compared to benzene or substituted arenes the nonplanar 1,2-dithiin is of much lower molecular symmetry, and therefore there are many more vibrational modes with the proper symmetry to be activated by ionization. The result is broad featureless ionization bands in the photoelectron spectra of 1,2-dichalcogenins.

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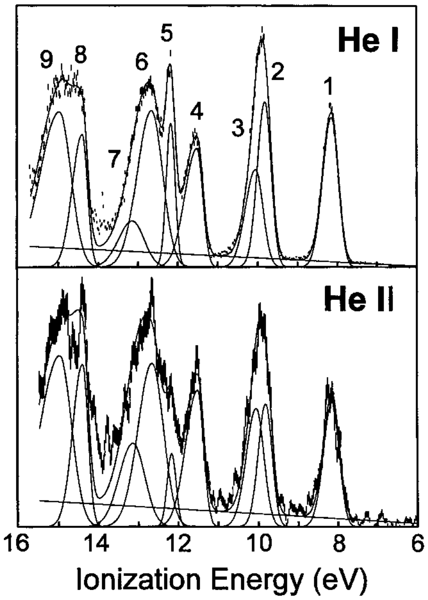

Figure 3. He I and He II photoelectron spectra of 1,2-dithiin.

Comparison of the He I and He II spectra of 1,2-dithiin shows that for the most part there are no large changes in the relative intensity of the ionizations, indicating that there is a large degree of mixing of sulfur and carbon character throughout the valence orbitals. Gaussian 3 does grow relative to Gaussians 1 and 2, consistent with the third highest occupied orbital containing more carbon character than the HOMO or SHOMO.

The only ionization that shows substantial change in relative energy in the He II spectrum is the sharp ionization labeled 5 at 12.17 eV. Gaussian 5 decreases substantially in the He II spectrum as compared to all of the other ionizations, indicating that this ionization corresponds to an orbital with a high degree of sulfur character. The only orbital that would be expected to have a substantial degree of sulfur character is the S−S σ bond, and calculations agree with this (vide infra). For comparison, the S−S σ bond ionization of dimethyl disulfide is located at 11.26 eV. The narrow shape of this band indicates that removal of an electron from this orbital does not substantially change the geometry of the molecule, and the implications of this observation follow in the Discussion section.

The overall assignment of the photoelectron spectrum of 1,2-dithiin is that ionization 1 is the ionization from orbital **A**, while ionization from orbitals **B** and **C** are under the band at 10 eV. The relative intensities of Gaussians 2 and 3 indicate that the low ionization energy side of the band is associated with the orbital that has the most sulfur character. It is difficult to say what the exact vertical ionization energies are because these two ionizations overlap so much, but the relative energies can be assigned and are consistent with the relative energy of the ionizations labeled **B** and **C** as shown in Figure 1. Ionization 4 is assigned to the most stable π/lone pair ionization (**D**), while ionization 5 is predominantly associated with the S−S σ bond. At higher ionization energy are the S−C, C−C, and C−H σ bond ionizations, which cannot be unambiguously assigned.

3,6-Dimethyl-1,2-dithiin. The He I and He II photoelectron spectra from 7 to 11.5 eV of 3,6-dimethyl-1,2-dithiin are shown in Figure 4. The addition of methyl groups has several effects on these spectra as compared to those of unsubstituted 1,2-dithiin. First, all of the ionizations have been destabilized from the position of the ionizations of 1,2-dithiin due to the electron-donating nature of the methyl groups. Second, the shape of the second ionization band, which is now centered at about 9.5 eV, is much different than the shape of the second band of 1,2-dithiin. The vertical ionization energies of the two ionizations under this band can now be seen clearly. The difference in shape is due to the fact that one of the ionizations is destabilized more than the other upon addition of the methyl groups, indicating that one of the two orbitals associated with these ionizations has more carbon character at the 3 and 6 positions than the other one. Gaussian 4 is also destabilized significantly from its position in the spectrum of 1,2-dithiin, consistent with a high degree of carbon π character and its assignment as the most stable π/lone pair orbital. The ionization associated with the S−S σ bond is not clearly observed for 3,6-dimethyl-1,2-dithiin because of the presence of ionizations associated with the C−H σ bonds of the methyl groups around 12 eV.

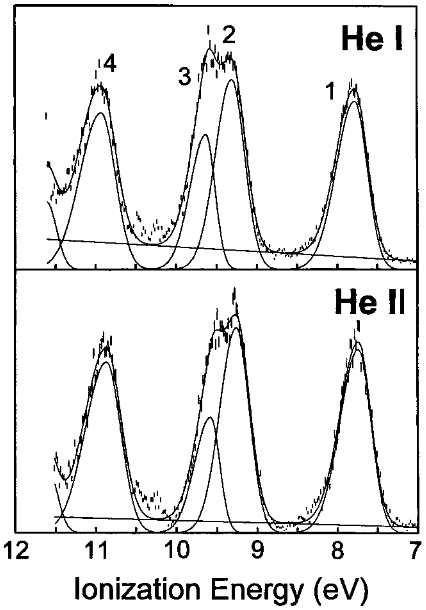

Figure 4. He I and He II photoelectron spectra of the first three ionization bands of 3,6-dimethyl-1,2-dithiin.

Comparison of the He I and He II spectra of 3,6-dimethyl-1,2-dithiin also shows some differences from what was observed for 1,2-dithiin. While for 1,2-dithiin, Gaussian 3 increases in relative area compared to 1 and 2, for 3,6-dimethyl-1,2-dithiin it is now Gaussian 2 that increases in relative area compared to 1 and 3. This indicates that ionization 2 for 3,6-dimethyl-1,2-dithiin is associated with an orbital that has more carbon character than ionizations 1 and 3. The addition of the methyl substituents has destabilized orbital **C** more than orbital **B** and the ionizations associated with these orbitals are now switched in relative energy compared to the assignment given for 1,2-dithiin. The assignment of the spectra of 3,6-dimethyl-1,2-dithiin is that ionization 1 is associated with orbital **A**, ionization 2 is associated with orbital **C**, ionization 3 is associated with orbital **B**, and ionization 4 is associated with orbital **D**.

3,6-Diisopropyl-1,2-dithiin and 3,6-Di-*tert*-butyl-1,2-dithiin. In addition to the He I spectra of 3,6-diisopropyl-1,2-dithiin and 3,6-di-*tert*-butyl-1,2-dithiin shown in Figure 2, the He I, He II, and Ne I photoelectron spectra of 3,6-diisopropyl-1,2-dithiin and the He I and Ne I photoelectron spectra of 3,6-di-*tert*-butyl-1,2-dithiin from 7 to 10 eV are available in the Supporting Information. Fit data are listed in Table 1. Similar to the spectra of 1,2-dithiin and 3,6-dimethyl-1,2-dithiin, the spectra of these two compounds each contain a band that is fit with one Gaussian and assigned to ionization from orbital **A**, and two Gaussians that are close in energy to each other and are assigned to ionization from orbitals **B** and **C**. Ionizations at

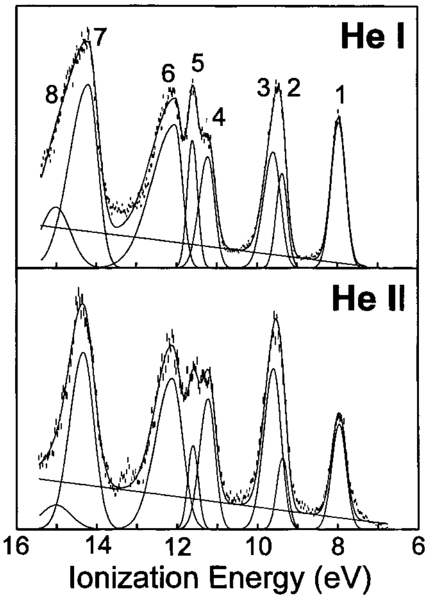

Figure 5. He I and He II photoelectron spectra of 1,2-diselenin.

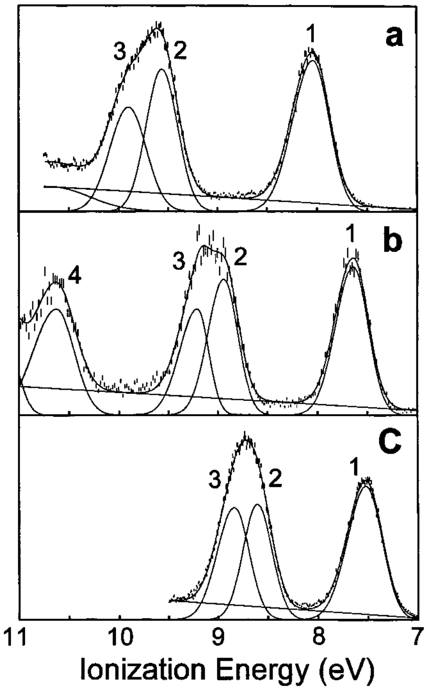

Figure 6. He I photoelectron spectra of (a) 2-selenathiin, (b) 3,6-dimethyl-1,2-diselenin, and (c) 3,6-di-*tert*-butyl-1,2-diselenin.

higher ionization energy such as the ionizations from orbital **D** and the S$-$S σ bond are now obscured by the presence of additional C$-$C and C$-$H σ bond ionizations from the substituents. The ionizations of the compounds with isopropyl and *tert*-butyl substituents are further destabilized from those of 1,2-dithiin or 3,6-dimethyl-1,2-dithiin, as expected as the total electron density donated to the molecule increases with these substituents.

For 3,6-diisopropyl-1,2-dithiin, Gaussian 2 increases in relative area to Gaussian 3 when the He II spectrum is compared to the He I spectrum, while the opposite trend is seen when the Ne I spectrum is compared to the He I spectrum. This would suggest that the ionization associated with the orbital with the most carbon character is at lower ionization energy, similar to what was observed for the methyl compound, and therefore suggests that the π/lone pair-based ionization energies decrease in the order **B** $>$ **C** $\gg$ **A**. For 3,6-di-*tert*-butyl-1,2-dithiin, however, Gaussian 2 *increases* in relative area compared to Gaussian 3, which would indicate that the π/lone pair-based ionization energies for 3,6-di-*tert*-butyl-1,2-dithiin decrease in the order **C** $>$ **B** $\gg$ **A**, the same assignment as for unsubstituted 1,2-dithiin. The change in relative energies of **B** and **C** observed for these compounds will be addressed in more detail in the Discussion section.

1,2-Diselenin, 3,6-Dimethyl-1,2-dithiin, 3,6-Di-*tert*-butyl-1,2-diselenin and 2-Selenathiin. The He I and He II photoelectron spectra of 1,2-diselenin from 6 to 16 eV are shown in Figure 5, and the He I photoelectron spectra from 7 to 11 eV of the other selenium-containing compounds studied are shown in Figure 6. Variable photon spectra for these compounds are given in Supporting Information, and fit data from all these spectra are again listed in Table 1.

As the sulfur atoms of the 1,2-dithiin are replaced by selenium atoms in 2-selenathiin and 1,2-diselenin, the ionizations are destabilized due to the lower ionization energy of Se 4p as compared to S 3p orbitals. The selenium lone pair ionizations of dimethyl diselenide, for example, are destabilized about 0.4 eV from the sulfur lone pair ionizations of dimethyl disulfide.[29,30] For 2-selenathiin, the lone pair orbitals will not have equal amounts of sulfur and selenium character. The LP_+ and LP_- orbitals for a Se$-$S fragment will be split further apart in energy with the more stable LP_+ orbital having a majority of S character and LP_- residing predominantly on the selenium atom.

The first ionization of 2-selenathiin is destabilized 0.13 eV from the first ionization of 1,2-dithiin. This shift and the destabilization of the other ionizations of 2-selenathiin and 1,2-diselenin will be described more fully in the Discussion section. In the He II spectrum as compared to the He I spectrum of 2-selenathiin, both Gaussians 2 and 3 increase in area compared to Gaussian 1. This would indicate increased chalcogen character in the HOMO of 2-selenathiin. The Ne I spectrum shows much smaller changes as compared to the He I spectrum, due to the smaller changes in relative cross sections of C 2p and Se 4p for He I and Ne I.

For 1,2-diselenin the first three ionizations are destabilized further from their positions for 2-selenathiin, and the additional higher-energy ionizations that are observed for 1,2-diselenin are also all destabilized from their position in 1,2-dithiin. Gaussian 1 and 2 both decrease significantly in the He II spectrum, indicating that the order for the first three ionizations of 1,2-diselenin is the same as for 1,2-dithiin. The ionization labeled 4 is assigned to the most stable π/lone pair ionization. The narrow Gaussian labeled 5 in the spectra of 1,2-diselenin is assigned primarily to the Se$-$Se σ bond ionization, which is destabilized 0.56 eV from the corresponding ionization of 1,2-dithiin. Ionization 5 decreases substantially in the He II spectrum, indicating that the associated orbital contains a high degree of Se$-$Se σ bond character, analogous to the primarily S$-$S σ bond orbital of 1,2-dithiin. At higher ionization energy are the Se$-$C, C$-$C, and C$-$H σ bond ionizations.

The spectra of 3,6-dimethyl-1,2-diselenin show the same trends that were observed for 3,6-dimethyl-1,2-dithiin. The ionizations have again been destabilized from the position of the ionizations of 1,2-diselenin, and the shape of the second ionization band is also different from the shape of the second band of 1,2-diselenin. Comparison of the He I and He II spectra

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Table 2. Comparison of Calculated[a] Geometric Parameters and Lowest Ionization Potentials with Experimental Data

parameter	1,2-dithiin (exptl)	1,2-dithiin (calcd)	3,6-dimethyl-1,2-dithiin
S−S bond, Å	2.05	2.07	2.07
S−C bond, Å	1.76	1.76	1.78
C=C bond, Å	1.35	1.36	1.36
C−C bond (in ring), Å	1.45	1.45	1.45
C−C bond (methyl), Å	−	−	1.50
SSC angle, °	98.7	97.8	98.3
SCC angle, °	121.4	122.0	119.5
CCC angle (in ring), °	124.2	123.9	125.3
CCC angle (methyl), °	−	−	124.4
CSSC torsion, °	53.9	54.8	56.6
SSCC torsion (in ring), °	−41.2	−42.6	−43.0
SSCC torsion (methyl), °	−	−	141.9
SCC torsion, °	0.3	1.6	1.5
CCCC torsion (in ring), °	29	28.0	28.4
CCCC torsion (methyl), °	−	−	176.1
ionization potential, eV	8.16	8.16	7.96 (7.78)[b]

[a] Calculations were done using MP2/6-31+G*. [b] Experimental value.

of 3,6-dimethyl-1,2-diselenin also shows that Gaussian 2 increases in relative area compared to 1 and 3, while Gaussian 3 increased in relative area compared to 1 and 2 for 1,2-diselenin. The conclusion is again that the addition of the methyl groups has destabilized orbital **C** more than orbital **B** and the ionizations associated with these orbitals are switched in relative energy compared to the assignment given for 1,2-diselenin, as was also seen in the case of the 1,2-dithiins. The He II spectrum of 3,6-di-*tert*-butyl-1,2-diselenin shows that both Gaussians 2 and 3 increase substantially in area compared to Gaussian 1, again indicating a large buildup of chalcogen character in the HOMO of the 1,2-diselenins as compared to 1,2-dithiins.

Computational Results

The geometry of 1,2-dithiin was optimized with a variety of methods (HF, MP2, and B3PW91) and basis sets 6-31G and 6-311G with every combination of polarization functions (*) and diffuse functions (+), and with LANL2DZ. Data from these calculations are tabulated in Supporting Information. The best geometry relative to the structure known from microwave spectroscopy[13] was reached with ab initio calculations with second-order Møller−Plesset perturbation using the 6-31G* basis set, but when the first vertical ionization energy was calculated by Δ*S*CF all basis sets that lacked diffuse orbitals gave results that differed from the experimental first ionization energy by up to 0.32 eV. As the best compromise between accurate neutral and cation radical predictions, the method/basis set MP2/6-31+G* was chosen and also used for calculations on 3,6-dimethyl-1,2-dithiin, with results listed in Table 2. The left-hand column on this table lists experimental geometric parameters for 1,2-dithiin from the microwave structure[13] and the experimental first ionization energy. The second column lists the theoretical values calculated for 1,2-dithiin. The theoretical ionization potential for 1,2-dithiin is identical to the experimental value to less than 0.01 eV. The global minimum calculated for 1,2-dithiin has a twisted geometry almost identical to the experimentally determined geometry, and the geometry of 3,6-dimethyl-1,2-dithiin is very similar.

The overall result of these calculations is that theory agrees well with the experimental geometry, ionization energies, and electronic structure as described by the photoelectron spectroscopic results. Contour plots for the filled molecular orbitals that are primarily carbon π and sulfur lone pair calculated with the 6-31+G* basis set are shown in Figure 7. A ball-and-spoke model of the molecule is also shown in the upper left-hand corner of the figure to illustrate the geometry and the orientation of the molecules in the contour plots. The orbitals calculated agree well with the simple description of the electronic structure of 1,2-dithiin described earlier. Each of the plots in Figure 7 are labeled with the orbital number from the calculation and the letter of the corresponding orbital in Figure 1. The main differences seen between the orbital plots in Figure 7 and the simplified schematics in Figure 1 are due to the nonplanarity of the molecule, which results in some perturbations, primarily that a significant overlap occurs between the upper lobe of one S 3p orbital with the lower lobe of the other S 3p orbital in all antiparallel combinations (HOMO and HOMO-1), creating a Möbius-type overlap that would be expected to stabilize an 8π electron molecule such as 1,2-dithiin. In agreement with what is observed in the photoelectron spectra, the calculated energies of these four orbitals fall in a 1:2:1 pattern, with calculated orbital energies of −8.32 eV, −10.43 eV, −10.46 eV, and −14.38 eV. As previously noted, the calculation predicts a different energy ordering of the orbitals labeled **B** and **C**, but does agree with the experiment that they are very close in energy to one another (0.03 eV splitting calculated). The calculation places the lowest-energy carbon π and sulfur lone pair orbital below the two S−C σ orbitals and the S−S σ orbital.

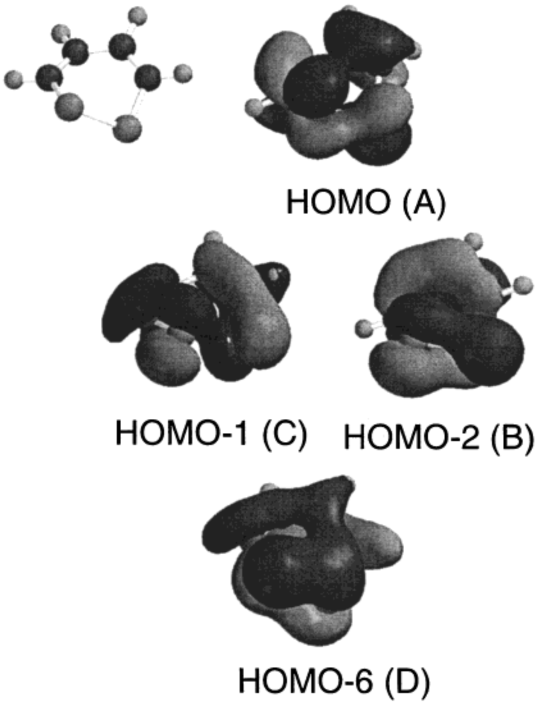

Figure 7. Density plots of the four filled π/lone pair orbitals of 1,2-dithiin as calculated by Spartan using the 6-31+G* basis set. The labels in parentheses indicate the corresponding orbital in Figure 1.

Discussion

The previous sections described the assignments of the photoelectron spectra for each of the compounds studied and showed that calculations reasonably agree with the experimental data. To briefly summarize the most important experimental results, the first four ionizations of each of these compounds, which correspond to removal of electrons from orbitals that are primarily carbon π and chalcogen lone pair in character, fall in a 1:2:1 pattern. Comparison of the spectra obtained with different photon energies indicates substantial mixing between the carbon π and chalcogen lone pairs, with chalcogen character

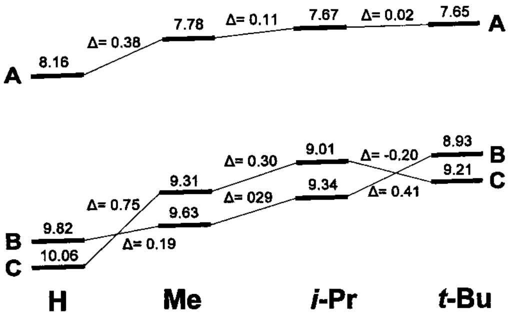

Figure 8. Correlation diagram showing the shifts in the first three ionizations as substituents are added to 1,2-dithiin.

decreasing in the order **B** > **A** ≈ **C** > **D**. The chalcogen character in **A** and **B** increases as sulfur is replaced by selenium. The ionization energies are affected by addition of substituents, and substituents can change the order of the ionizations from orbitals **B** and **C**. Additional insight can be gained by analyzing the shifts of these ionizations that occur with different substituents. These shifts will be discussed in the following section in terms of the effects of substitution on the 1,2-dithiin ring, and in terms of the effects of substitution of selenium for sulfur in the ring. The photoelectron spectra of 1,2-dithiin and 1,2-diselenin also contain a sharp ionization that is associated primarily with the chalcogen−chalcogen σ bond. The last portion of this section will describe how a combination of experimental and computational results gives insight into the likely cause of the unusual color of these compounds.

Effect of Substituents on the Photoelectron Spectra of 1,2-Dithiins. The trends in the ionization energies of the three lowest-energy ionizations as substituents are added to 1,2-dithiin are shown schematically in the correlation diagram depicted in Figure 8. The overall trend for all ionizations is that they are destabilized as the electron-donating ability of the alkyl group to sp^2-hybridized carbon increases. For 3,6-dimethyl-1,2-dithiin, ionizations from orbitals **A** and **C** are destabilized more than **B** from the position of these ionizations in the spectra of 1,2-dithiin. The primary cause of the destabilization of the ionization of 3,6-dimethyl-1,2-dithiin is the hyperconjugative interactions that can occur between the methyl e symmetry C−H σ-bond orbitals and the π orbitals of the 1,2-dithiin ring, and the magnitude of the shift gives an indication of the amount of electron density at the 3 and 6 positions for a particular orbital. The larger shift of **A** and **C** than **B** is consistent with the assignment given, as the simple schematics of the orbitals shown in Figure 1 indicate that orbitals **A** and **C** have large contributions at the 3 and 6 positions, while **B** will be more evenly distributed over carbons 3, 4, 5, and 6 and also has a relatively high degree of sulfur character. This effect is enough to switch the relative ordering of the ionizations from orbitals **B** and **C**. Orbital **A** is not destabilized as much as orbital **C**, consistent with orbital **A** having slightly more sulfur character than orbital **C** and also having poorer energy match with the hyperconjugative methyl orbital.

For 3,6-diisopropyl-1,2-dithiin all of the ionizations are further destabilized from their positions in the spectrum of 3,6-dimethyl-1,2-dithiin. For 3,6-di-*tert*-butyl-1,2-dithiin it was noted above that the order of the ionizations from orbitals **B** and **C** has reverted to the order seen for 1,2-dithiin. Methyl and isopropyl both have the possibility of a hyperconjugative interaction through their α C−H σ bond orbitals with the dithiin orbitals that have π character at the 3 and 6 positions, while a *tert*-butyl substituent is an electron donor only in an inductive manner and will affect all the dithiin orbitals equally. There is also the possibility that the bulkier *tert*-butyl substituents cause differences in ring geometry that could also cause a change in the ordering of these two orbitals that are close in energy.

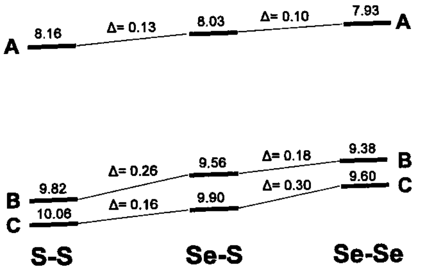

Figure 9. Correlation diagram showing the shifts in the first three ionizations from 1,2-dithiin to 2-selenathiin to 1,2-diselenin.

Comparison of 1,2-Dithiin, 2-Selenathiin, and 1,2-Diselenin. The trends in the ionization energies of the three lowest-energy ionizations as the sulfurs are replaced by seleniums are shown schematically in the correlation diagram in Figure 9. The total shift of the first ionization from 1,2-dithiin to 1,2-diselenin is 0.23 eV. For comparison, the first ionization of the peri-chalcogen-bridged naphthalene compounds for which photoelectron spectra have been reported by Bock[28] only shift by 0.08 eV from the dithiin to diselenin, which would indicate that the highest occupied molecular orbitals for the naphthalene compounds contains significantly less chalcogen character than the 1,2-dichalcogenins studied here. The total shift of ionizations 2 and 3 from 1,2-dithiin to 1,2-diselenin is the same within experimental error. Ionization 2 feels the majority of the effect of the first selenium substitution and is destabilized more than ionization 3 when one sulfur is replaced by selenium, but ionization 3 then feels the majority of the effect of the second selenium substitution and "catches up" to ionization 2.

It is also interesting to compare the ionization shifts observed upon 3,6-substitution of 1,2-dithiin to the ionization shifts of 1,2-diselenin when the same substituents are added. Comparison of the photoelectron spectra of 3,6-dimethyl-1,2-diselenin, 3,6-di-*tert*-butyl-1,2-diselenin and 1,2-diselenin shows the expected destabilization of ionizations of the first two compounds. However, the substituents do not effect the ionization energy as much for the 1,2-diselenins as for the 1,2-dithiins. This is because the HOMO of 1,2-diselenin has less carbon π character than the HOMO of 1,2-dithiin, which is most likely due in large part to the poorer energy match between the Se fragment orbitals and the carbon π fragment orbitals than between analogous sulfur and carbon orbitals.

Explanation of the Color of 1,2-Dichalcogenins. As described in the Results section, the photoelectron spectrum of 1,2-dithiin contains a very sharp ionization located at 12.17 eV that can be assigned to an orbital of primarily sulfur character because the intensity of the ionization drops substantially in the He II spectrum. The theoretical results indicate that the only orbital expected to contain a high amount of sulfur character in this energy region is primarily associated with the sulfur−sulfur σ bond. A contour plot of this orbital is shown in the left side of Figure 10, which illustrates the high degree of sulfur character and S−S σ bonding associated with this orbital. The width of an ionization band is directly related to the amount of bonding or antibonding character associated with an orbital.[17] Sharp ionization bands are observed because removal of an electron from a weakly bonding or antibonding orbital does not greatly change the molecular geometry. The primary geometry change upon removal of an electron from this highly localized orbital would be expected to involve lengthening of the S−S bond.

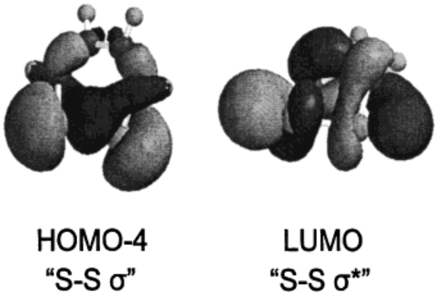

Figure 10. Density plots of the S−S σ and S−S σ^* orbitals of 1,2-dithiin as calculated by Spartan with the 6-31+G* basis set.

Table 3. Transition Energies for 1,2-Dithiin Calculated by the CI-Singles Method

symmetry	excited state	predicted wavelength[a]	exptl absorption maxima[a] (molar absorptivity)[b]
	$\pi \rightarrow \sigma^*$ (HOMO → LUMO)		
B	T_1	605	452 (90)
	S_1	354	
	$\pi \rightarrow \sigma^*$ (HOMO-1 → LUMO)		
B	T_2	357	279 (2000)
	S_2	237	
	$\pi \rightarrow \sigma^*$ (HOMO-2 → LUMO)		
A	T_3	332	248 (1500)
	S_3	225	

[a] nm. [b] L/mol·cm.

The contour plot in Figure 10 shows that the shared electron density is not directly between the two sulfur atoms, which would be expected to result in a weakening of the S−S σ bond. Consequently, this ionization for 1,2-dithiin is much more narrow than is seen for ionization of other predominantly sulfur−sulfur σ orbitals. For example, the corresponding S−S σ ionization of dimethyl disulfide measured under the same instrument conditions gives an average full-width-at-half-height of 0.38 eV, while for 1,2-dithiin it is 0.26 eV. The Se−Se σ bond ionization of 1,2-diselenin is also narrow, with an average full-width-at-half-height of 0.30 eV.

The observation of experimental evidence for a weak S−S σ bond should not be construed as experimental evidence that the overall thermodynamic S−S bond strength for 1,2-dithiin is less than for other disulfides. Many of the other valence orbitals, in particular the four filled π/lone pair orbitals that have been discussed, contribute additional S−S bonding character. However, the significance of a chalcogen−chalcogen σ orbital with weak bonding character is that a correspondingly weakly antibonding σ^* orbital would be expected at lower energy than for a typical dichalcogenide. The presence of a low-energy σ^* orbital, combined with a HOMO that is destabilized compared to a typical dichalcogenide, could result in the low-energy electronic absorption that causes the unusual color of these compounds.

The computational results for 1,2-dithiin indicate that the ground state LUMO, which is shown in the contour plot on the right side of Figure 10, is an orbital that is also highly localized on the sulfur orbitals and is primarily S−S σ^* in character. This orbital is located at +1.29 eV in these calculations, while a similar calculation on dimethyl disulfide places the S−S σ^* orbital as the LUMO+2 orbital at +2.37 eV, 1.08 eV higher in energy. Additional calculations were performed to predict the electronic transitions of 1,2-dithiin using the single-excitation configuration interaction method[22] and the 6-31+G* basis set. Results from calculations of the three lowest-energy singlet and triplet electronic transitions using the CIS method are given in Table 3 and agree reasonably well with values for the singlet transitions previously calculated with the CIPSI method.[8] Results are tabulated in greater detail in Supporting Information. These calculations show that the first excited singlet and triplet states (S_1 and T_1) are primarily excitation from the HOMO to the LUMO.[31] The predicted wavelength of these transitions fit fairly well with the observed absorption maxima in the UV−visible spectrum of 1,2-dithiin. The differences of the calculated transition values from experimental values are within the range found with the CIS method for small molecules such as ethylene, formaldehyde, or pyridine.[22] The lowest-energy transition for 1,2-dithiin is calculated to be to the triplet state, which is in agreement with the small extinction coefficient ($\epsilon = 90$)[14] observed for the absorption in the visible region of the spectrum.[32] In terms of the primary character of the orbitals described by the photoelectron spectra and calculations, the transition in the visible region can be described as a π/lone pair-to-σ^* type transition. An analogous CIS calculation was also performed for dimethyl disulfide, and found that the lowest-energy transition is a forbidden transition at 273 nm with primarily lone pair-to-σ^*_{S-S} character. The calculation is consistent with the observed lowest-energy transition in the UV−visible spectrum of dimethyl disulfide at 254 nm. This absorption has a small extinction coefficient ($\epsilon = 275$)[33] consistent with a forbidden transition.

Our suggestion that the low-energy transition, resulting in the red color of 1,2-dithiin, is a HOMO → σ^*_{S-S} transition may be relevant to other colored disulfides. As examples, 1,2-dithietanes are yellow with absorption maxima at 426 nm,[34] and 1,2-dithiiranes are red with absorption maxima at 452 nm.[35] The transition in these cases may involve lone pair-to-σ^*_{S-S} transitions which have unusually low energy due largely to low-energy σ^* orbitals. CIS calculations utilizing MP2/G-31+G* optimized geometries and geometry and frequency calculations of the excited states support this conclusion (see Supporting Information for details). For dithiirane and 1,2-dithietane, the following transitions were found: for dithiirane, 534 nm forbidden triplet and 393 nm allowed singlet; for 1,2-dithietane, 513 nm forbidden triplet and 380 nm allowed singlet. All these transitions are lone pair-to-σ^*_{S-S}.

Conclusions

To summarize, the photoelectron spectra reported here for 1,2-dichalcogenins indicate that there is a large degree of mixing of chalcogen and carbon character through most of the valence orbitals. The ionization energies of these compounds show a strong dependence on substituents and the chalcogen. The highest occupied molecular orbitals of the selenium-containing compounds are more localized on the chalcogen than the highest occupied molecular orbital of 1,2-dithiins, due to poorer energy matching between selenium 4p and carbon 2p atomic orbitals than for sulfur 3p and carbon 2p atomic orbitals. The photo-

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[31] Geometry optimizations were also performed on the first singlet and triplet excited states of 1,2-dithiin. In these excited states there is a substantial lengthening of the S−S bond length and a lowering of the S−S stretching frequency (see Table 5 in the Supporting Information), which is further proof that the transition in the visible region involves an excited state with significant occupation of a S−S antibonding orbital.

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electron spectra of 1,2-dithiin and 1,2-diselenin give experimental evidence for a chalcogen−chalcogen σ bond orbital with relatively weak bonding character as compared to other dichalcogenides. Calculations show that an orbital that is primarily S−S σ^* in character is the lowest unoccupied molecular orbital of 1,2-dithiin, and electronic transition calculations reveal a low-energy HOMO-to-LUMO transition that can be described as a π/lone pair to σ^* transition that explains the unusual color of 1,2-dichalcogenins.

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Note Added in Proof: The theoretical calculations reported are in substantial agreement with DFT calculations independently reported by J. Fabian (Fabian, J.; Mann, M.; Petiau, M. *J. Mol. Model.* **2000**, *6*, 177−185). X-ray crystallographic studies on 3,6-di-*tert*-butyl-1,2-dithiin (**1f**) show that it has a different geometry in the solid state than 1,2-dithiin (**1c**) has in the gas phase as determined by microwave spectroscopy. Thus, compound **1f** shows an in-ring C−C−C−C dihedral angle of 0.4° and a C−S−S−C dihedral angle of 62.2°; for compound **1c** the corresponding angles are 29° and 53.9°, respectively. Full details of the structure of **1f** will be presented elsewhere.

Supporting Information Available: Tables with calculated geometric parameters, ionizations potentials, and spin-squared values for 1,2-dithiin; calculated geometric parameters of 3,6-dimethyl-1,2-dithiin, dithiirane and dithietane; calculated molecular orbitals energies of disulfides; and calculated electronic transitions for disulfides. Figures with variable photon energy photoelectron spectra of 3,6-diisopropyl-1,2-dithiin, 3,6-di-*tert*-butyl-1,2-dithiin, 2-selenathiin, 3,6-dimethyl-1,2-diselenin, and 3,6-di-*tert*-butyl-1,2-diselenin (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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